

Van der Waals Energies in Density Functional Theory

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In principle, density functional theory yields the correct ground-state densities and energies of electronic systems under the action of a static external potential. However, traditional approximations fail to include Van der Waals energies between separated systems. This paper proposes a practical procedure for remedying this difficulty. Our method allows seamless calculations between small and large inter-system distances. The asymptotic H-He and He-He interactions are calculated as a first illustration, with very accurate results.

Density functional theory (DFT) [1] has become a useful tool for calculating ground-state energies and density distributions of atoms, molecules and solids, particularly of systems consisting of *many* atoms [2]. The simplest approximation for practical purposes is the local-density approximation (LDA) [3], based on the properties of the uniform electron gas. The so-called generalized gradient approximations (GGA) are important refinements of the LDA.

In principle DFT yields the exact ground state energy, including long-range Van der Waals (VdW) energies, very important in organic chemistry and elsewhere. However the commonly used LDA and GGA, designed for non-uniform electron gases, fail to capture the essence of VdW energies. The latter reflect correlated motions of electrons due to the Coulomb interactions between distant, even non-overlapping atoms, molecules and solids. Thus a new strategy is needed.

Here we propose a first-principles approach, which contains the following essential ingredients: 1. The density distribution, $n(r)$, is approximated by the LDA or GGA. 2. The Coulomb interaction is divided into short and long range parts, of which only the latter contributes to VdW energies. 3. The contribution of the long-range interactions to the energy is expressed by the so-called adiabatic connection formula (see Eq.(8) below). 4. This expression is transformed into the time-domain, avoiding the need to solve a self-consistent equation for the density-density response function. As an illustration we calculate the asymptotic VdW interaction between two Helium atoms and between Hydrogen and Helium atoms, with excellent results. The method allows seamless calculation of the interaction of two subsystems, e.g., an atom and a surface, from small to large separations. Our work was carried out independently and differs substantially from recently published work by Anderssen et al [5] and by Hult et al. [6], which depend critically on a fitting parameter.

Since the VdW energies are due to the long range of the electron-electron interaction, $U(r) = 1/r$, we separate this interaction, as a preliminary step, into short and long range parts,

$$U(r) = U_{sr}(r) + U_{lr}(r). \quad (1)$$

For example, we can choose $U_{sr}(r) \equiv e^{-\kappa r}/r$, with κ^{-1} chosen somewhat larger than a typical intra-atomic

electron-electron distance, so that the effect of U_{lr} on the total energy is small. The calculated total energy is, in principle, independent of the choice of κ , in practice — with appropriate approximations — nearly so.

We now write the Hamiltonian as a function of a coupling constant, λ , that “turns on” U_{lr} , such that the physical Hamiltonian operator corresponds to $\lambda = 1$:

$$\mathcal{H}(\lambda) = T + V_\lambda + U_{sr} + \lambda U_{lr}, \quad 0 \leq \lambda \leq 1 \quad (2)$$

where T is the kinetic energy, and the external potential V_λ is chosen such that the ground state density $n_\lambda(r)$ of $\mathcal{H}(\lambda)$ equals the exact physical density $n_{\lambda=1}(r)$ for all λ [4]. Note that for $\lambda = 0$, the interaction is entirely short range and that for $\lambda = 1$, $V_{\lambda=1} = V_{\text{ext}}$. We denote the ground state energy of $\mathcal{H}(\lambda)$ by $E(\lambda)$. Then the ground-state energy of the physical system, $E \equiv E(1)$, is given by

$$E = E(0) + \int dr [V_{\text{ext}}(r) - V_0(r)] n(r) + \frac{1}{2} \int dr dr' U_{lr}(r - r') \left[\int_0^1 \langle \hat{n}(r) \hat{n}(r') \rangle_\lambda d\lambda - n(r) \delta(r - r') \right], \quad (3)$$

where \hat{n} is the density operator; $V_0(r)$, defined above, eventually drops out; see Eq.(5).

From DFT, $E(0)$ is given by

$$E(0) = T_s[n(r)] + \int dr V_0(r) n(r) + \frac{1}{2} \int dr dr' U_{sr}(r - r') n(r) n(r') + E_{xc}^{sr}[n(r)], \quad (4)$$

where $T_s[n(r)]$, is the non-interacting kinetic energy functional and $E_{xc}^{sr}[n(r)]$ is the exchange correlation energy of an electron gas with density $n(r)$ and the short range interaction U_{sr} .

Substituting (4) in (3) we find, after simple manipulations, the exact result (independent of the form of U_{lr}):

$$E = T_s[n(r)] + \int dr V_{\text{ext}}(r) n(r) + \frac{1}{2} \int dr dr' U(r - r') n(r) n(r') + E_{xc}^{sr}[n(r)] - U_{lr}(0)N + E_{pol}[n(r)] \quad (5)$$

where N is the number of electrons, and

$$E_{pol} \equiv \frac{1}{2} \int dr dr' U_{\ell r}(r - r') \times \int_0^1 d\lambda \langle (\hat{n}(r) - n(r))(\hat{n}(r') - n(r')) \rangle_\lambda. \quad (6)$$

E_{pol} includes the long-range polarization energies.

To calculate the first four terms in Eq.(5) we use traditional methods. Experience [2] has shown that the density $n(r)$ may be calculated to a very good approximation by the LDA with the full $U(r)$. Such a calculation also automatically yields an approximate $T_s[n(r)]$,

$$T_s[n] = \sum_{j=1}^N \epsilon_j - \int v_{KS}(r) n(r) dr, \quad (7)$$

where v_{KS} is the Kohn-Sham (KS) effective potential that reproduces $n(r)$, and the ϵ_j are the single-particle energies available from the LDA calculation. For $E_{xc}^{sr}[n(r)]$ there exist unpublished excellent results in the LDA [7].

To evaluate E_{pol} we use the appropriate exact connection formula [4],

$$E_{pol} = - \int dr dr' U_{\ell r}(r - r') \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{4\pi} \text{Im} \chi(r, r'; \omega, \lambda), \quad (8)$$

where the linear-response susceptibility χ is defined, as usual, as follows. Let $\alpha V_1(r, \omega) e^{-i\omega t}$ be a small perturbing potential, acting on the ground state of $\mathcal{H}(\lambda)$, and producing a density response $\alpha n_1(r, \omega) e^{-i\omega t}$, where α is infinitesimal. Then χ is defined by

$$n_1(r, \omega) = \int dr' \chi(r, r'; \omega, \lambda) V_1(r', \omega). \quad (9)$$

For $\lambda = 1$, methods to evaluate $\chi(r, r'; \omega, \lambda)$ have been discussed in the past [8,9], and can be formally carried over to $\lambda < 1$. χ is the solution of the integral equation:

$$\chi(r, r'; \omega, \lambda) = \chi_{KS}(r, r'; \omega) + \int dr'' dr''' \chi_{KS}(r, r''; \omega) \times [U(r'' - r''') + f_{xc}(r'', r'''; \omega, \lambda)] \chi(r''', r'; \omega, \lambda), \quad (10)$$

where $\chi_{KS}(r, r'; \omega)$ is the response function of the corresponding non-interacting Kohn-Sham system, and f_{xc} describes exchange and correlation effects (see Eq.(6) of Ref. [9]).

However, except for systems of very high symmetry, such as spherical atoms, the self-consistent solution of (10) is computationally very forbidding. Here we propose an equivalent but much less cumbersome procedure, which avoids the solution of a self-consistent integral equation for each value of λ . We note that $\chi(r, r'; \omega, \lambda)$ is the Fourier transform, $\chi(r, r'; \omega, \lambda) = \int dt \chi(r, r'; t, \lambda) e^{i\omega t}$, of the *time-dependent* response function, $\chi(r, r'; t, \lambda)$, defined as follows:

$$n_1(r, t, \lambda) = \int dr' dt' \chi(r, r'; t - t', \lambda) V_1(r', t'), \quad (11)$$

where $V_1(r', t)$ and $n_1(r, t, \lambda)$ are, respectively, external perturbing potential and density response. Eq.(8) can be rewritten as

$$E_{pol} = - \frac{1}{4\pi} \int dr dr' U_{\ell r}(r - r') \int_0^1 d\lambda \int_0^\infty \frac{dt}{t} \chi(r, r'; t, \lambda). \quad (12)$$

Following Gross and Kohn [9], we can replace the density response of the physical system to the external perturbing potential by the response of the (λ - independent) KS system to an effective potential,

$$n_1(r, t, \lambda) = \int dr' dt' \chi_{KS}(r, r'; t - t', \lambda) V_1^{eff}(r', t', \lambda), \quad (13)$$

where

$$V_1^{eff}(r', t', \lambda) = V_1(r', t') + V_{1,xc}(r', t', \lambda) + \int dr'' [U_{sr}(r' - r'') + \lambda U_{\ell r}(r' - r'')] n_1(r'', t, \lambda). \quad (14)$$

$V_{1,xc}(r', t', \lambda)$ is defined by Eqs.(13) and (14). Thus $\chi(r, r'; t, \lambda)$ is the density response of the non-interacting KS system at time t , to the $V_1^{eff}(r', t', \lambda)$ at $0 \leq t' \leq t$, induced by an external potential $V_1(r'', t') = \delta(r'' - r)\delta(t)$.

To complete this procedure we need a practical approximation for $V_{1,xc}$, for which, following Ref. [8], we set

$$V_{1,xc}(r', t', \lambda) = \left. \frac{\partial V_{xc}(n, \lambda)}{\partial n} \right|_{n_0(r')} n_1(r', t', \lambda), \quad (15)$$

where n_0 is the unperturbed density and V_{xc} is the static exchange-correlation potential in the LDA. Here, in addition to the usual approximation of the LDA, the frequency dependence (or retardation) of V_{xc} is neglected.

The evaluation of χ now requires the calculation of the evolution of the non-interacting KS system under the action of $V_1^{eff}(r', t', \lambda)$. At this point it is convenient to change from the coordinate representation to an orthonormal basis, $f_n(r)$, and write generically for any $F(r)$ and $G(r, r')$

$$F(r) = \sum_{m=1}^{\infty} F_m f_m(r) \\ G(r, r') = \sum_{m, m'=1}^{\infty} G_{m m'} f_m(r) f_{m'}(r'). \quad (16)$$

Thus Eq.(11) becomes

$$n_{1,m}(t, \lambda) = \int_0^\infty dt' \sum_{m'} \chi_{KS, m m'}(t - t'; \lambda) V_{1, m'}^{eff}(t', \lambda). \quad (17)$$

The following steps need to be carried out for each value of λ : 1. At time $t = 0^-$ the KS system is given by

the determinant $(N)^{-1} \text{Det} |\phi_1 \phi_2 \dots \phi_N|$ of the occupied KS orbitals ϕ_j . 2. At time 0^+ , after the action of a small external perturbation, $V(r) = \alpha f_m(r) \delta(t)$ (α small), each of the KS orbitals is changed, $\phi_j(r, t) \rightarrow \phi_j(r, t) - i\alpha f_m(r) \phi_j(r, t)$. (Effects on the orbitals of the finite unperturbed KS Hamiltonian and of the induced parts of V^{eff} in the infinitesimal interval $(0^-, 0^+)$ are negligible). 3. For $t > 0^+$ we integrate the time-dependent Schrödinger equation for each ϕ_j in a step-wise fashion, evaluating the first-order induced density $\alpha n_{1,m}(r, t) = \sum_j |\phi_j(r, t)|^2 - n_0(r)$ at each time step, to be able to compute the induced parts of V_1^{eff} (Eq.(14)), which depend on $n_{1,m}(r, t)$. 4. The projection of $n_{1,m}$ on $f_{m'}$ gives $\chi_{m m'}(t)$,

$$\chi_{m m'}(t) = (f_{m'}, n_{1,m}(t)). \quad (18)$$

From Eq.(12), we obtain

$$E_{pol} = -\frac{1}{4\pi} \int_0^\infty \frac{dt}{t} \int_0^1 d\lambda \sum_{m, m'} \chi_{m m'}(t, \lambda) U_{\ell r; m m'}. \quad (19)$$

In practice, the integration over λ is replaced by a finite sum.

As a simple example of this general procedure, we now apply it to the calculation of the asymptotic VdW interaction of a pair of spherically symmetric atoms. We denote the atoms by A and B , and their nuclear coordinates by R_A and R_B (taken to be on the z -axis), and write $R = |R_A - R_B|$. We take $R \gg a_A + a_B$, the sum of the atom radii and $\kappa \simeq (Ra)^{-1/2}$, where a is the atomic radius. The asymptotic VdW interaction is obtained from those parts of E_{pol} (Eq.(6)) in which r and r' are in different atoms. Take r to be in A and r' in B . Next we write $U = U_{sr} + \lambda U_{\ell r}$. Since $\kappa \rightarrow 0$ when $R \rightarrow \infty$, $U_{\ell r}$ can be treated as a small perturbation, giving to first order

$$\begin{aligned} \chi(r, r'; \omega, \lambda) &= \lambda \int dr_1 dr_2 U_{\ell r}(r_1 - r_2) \\ &\times \chi_A(r, r_1; \omega) \chi_B(r_2, r'; \omega), \end{aligned} \quad (20)$$

where $\chi_A(\chi_B)$ is the response of the isolated atom A (B). The integration over λ is now trivial. Lastly, we expand $U_{\ell r}(r - r')$ in $1/R$ and obtain the final expression, $E_{VdW} = -C_6/R^6$,

$$\begin{aligned} C_6 &= \frac{3}{\pi} \text{Im} \int_0^\infty d\omega \chi_A^{zz}(\omega) \chi_B^{zz}(\omega) \\ &= \frac{3}{\pi} \int_0^\infty dt_1 \int_0^\infty dt_2 \frac{\chi_A^{zz}(t_1) \chi_B^{zz}(t_2)}{t_1 + t_2}. \end{aligned} \quad (21)$$

In the above χ^{zz} is defined as the z -component of the density response to a perturbation in the z -direction, $\chi^{zz} = \int dr_1 dr_2 \chi(r_1, r_2) z_1 z_2$. The first form is well known, the second its Fourier transform into the time domain.

We have calculated the time-dependent response for the Helium atom in DFT as follows. We begin with the

exact $V_{xc}(r)$ [12], which reproduces the exact ground-state density $n_0(r)$ (known from highly accurate independent calculations), and the corresponding exact KS ground-state wavefunction ϕ_0 and energy ϵ_0 . We take as perturbation $V_1(r, t) = -\alpha z \delta(t)$. At time $t = 0^+$ the wavefunction will be

$$\phi(r, t = 0^+) = \phi_0(r) - i\alpha z \phi_0(r), \quad (22)$$

a combination of s- and p-like functions. For $t > 0$, we solve the time-dependent Schrödinger equation for $\phi(r, t) \equiv \phi_0(r, t) + \alpha \phi_1(r, t)$, with the initial condition (22). Linearizing in α gives the following equation for ϕ_1 :

$$\begin{aligned} i \frac{\partial \phi_1(r, t)}{\partial t} &= \mathcal{H}_0 \phi_1(r, t) + \mathcal{H}_1(t) \phi_0(r, t), \\ \phi_1(r, 0^+) &= -ir \phi_0(r) \end{aligned} \quad (23)$$

where $\phi_0(r, t) = e^{-i\epsilon_0 t} \phi_0(r)$, \mathcal{H}_0 is the KS unperturbed Helium Hamiltonian,

$$\mathcal{H}_1(t) = \int dr' \frac{n_1(r', t)}{|r - r'|} + \left. \frac{\partial V_{xc}}{\partial n} \right|_{n_0(r)} n_1(r, t), \quad (24)$$

and $n_1(r, t) = 4Re[\phi_0(r, t) \phi_1^*(r, t)]$. V_{xc} was calculated using the parameterization of Vosko et al. [13]. This equation was solved by stepwise integration in time. The time evolution from t to $t + \Delta t$ was carried out using the fast Fourier transform method as used in Ref. [14]. Since at each instant ϕ_1 evolves under the action of the total effective potential, the resulting response function $\chi(t)$ (and, if desired, the corresponding $\chi(\omega)$) is automatically self-consistent *without the need to first solve a self-consistent integral equation*, as is the case in the direct evaluation of $\chi(\omega)$ (see Eq.(10)).

In practice, the direct evaluation of the time integral in (21) is inconvenient because $\chi(t)$ oscillates with undiminishing amplitude at large t . We have therefore noted that if we define $\alpha(u) = \int_0^\infty \chi^{zz}(t) e^{-ut} dt$ (i.e. $\alpha(u) = \chi^{zz}(i\omega)$), the VdW coefficient, C_6 , can be written as

$$C_6 = \frac{3}{\pi} \int_0^\infty du \alpha_A(u) \alpha_B(u). \quad (25)$$

For helium $\chi(t)$ was calculated up to $t = 15$ atomic units (AU), which allows accurate calculation of $\alpha(u)$ for $u > u_0 = 0.4$. In the interval $0 \leq u \leq u_0$, we represented $\alpha(u)$ by the expression $a + b/(1 + cu^2)$, and fitted a, b, c to $\alpha(u)$ and its first two derivatives at $u = u_0$. (We checked that the results are insensitive to the exact choice of u_0 or to the choice of the extrapolating function). Fig. 1 shows our $\alpha(u)$ for He. The correct asymptotic form, $\alpha(u) \rightarrow 2/u^2$ (the f-sum rule), is automatically obeyed. The completeness sum rule, requires $\int_0^\infty \alpha(u) du = 2\pi < \phi_0 | z^2 | \phi_0 > \simeq 2.50$. Our $\alpha(u)$ gives 2.33. An independent check on our $\alpha(u)$ is the static susceptibility $\alpha(0)$. The best theoretical value is 1.383241 [15], while we find 1.38.

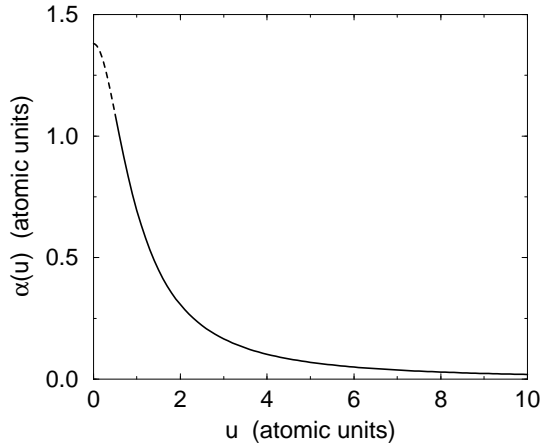


Fig. 1. The imaginary-frequency susceptibility $\alpha(u)$ for Helium (solid line - direct evaluation, broken line - extrapolation).

Our results for the He-He VdW constant is $C_6 = 1.45$, almost identical to the best theoretical value [16] 1.458. For the H-He system we find $C_6 = 2.81$ compared to the best theoretical value [17] of 2.817.

We feel cautious about the significance of the high accuracy of our results for the He-He and the H-He systems in view of the fact that our calculated $\alpha(u)$ leads to a 7% error in the completeness sum rule. At the same time our results demonstrate the soundness and feasibility of our approach. We are optimistic that our approach will not only give asymptotic van der Waals coefficients, but the entire nuclear potential energy function $\epsilon(R)$, including polarization energies.

We found that the results are rather sensitive to the choice of a good KS potential for the unperturbed ground state. Repeating the calculation by replacing the exact V_{xc} by V_{xc} in the local density approximation, the result for C_6 of the He-He system was 1.85, 28% too high. This is qualitatively similar to the experience of Petersilka et al. [18] with calculations of excited-state energies.

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